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(56) Documents Cited

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(58) Field of Search

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(54) Method and materials for the manufacture of moulds and refractory articles

(57) Moulds, especially for the casting of metals, and other articles, are made by forming a settable slurry of a refractory aggregate, one or more phosphates and fusible fibres and forming the mould by allowing the slurry to set in a mould. The fibres may be melted out from the formed product to enhance the porosity thereof. A castable magnesia system is also disclosed which comprises a short chain sodium, potassium or calcium phosphate or an equivalent phosphate.

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IMPROVEMENTS IN REFRACTORIES AND MOULD MAKING

The Shaw process of Precision Casting metals into ceramic moulds is described variously but particularly in U.K. Patents Nos. 716,394 and also 741,381. It should be noted that the continued success of this process for making large castings such as die castings continues 40 years on. Patent 716,394 using ethyl silicate as the binder is substantially unchanged. The key to its success is the principle of rapid ignition and microcrazing the ceramic to create dimensional stability and subsequent permeability.

With increasing need to meet requirements of health and safety the use of volatile substances to create microcrazing becomes more difficult. In addition the cost of these volatiles is not significant in the cost of the process.

Patent 741,381 describes an alternative which has not proved so popular - largely we believe because of the need to heat to achieve the desired microcrazing.

A further difficulty is encountered in the need in many modern steels or high melting point alloys to avoid the presence of silica.

The new process in accordance with the invention addresses each of the problems and sets out to provide a process that avoids the use of a volatile, a process that avoids ignition the use of high temperature heating
5 in order to generate stable and permeable mould and a process that avoids the need for a silicate binder.

The process of the present invention uses a neutral ph liquid phosphate mixture essentially monosodium phosphate
10 with the small addition of one or a combination of the following:- dipotassium phosphate, tetra potassium phosphate and dicalcium phosphate.

These additions move the ph to a figure of between 6 and
15 7 when used in conjunction with basic ceramics and encourages more mobile slurries for a given quantity of fluid. The solution preferred has been typically a 40% solution wgt with water of 3 parts of monosodium phosphate and 2 parts of dipotassium phosphate.

20

This mixture gives an effective strong gel within the parameters of the Shaw process - 2 minutes to about 20 minutes with a fast build up of ceramic mould strength. Suitable moulds can however be made using disodium
25 phosphate dipotassium phosphate or non calcium phosphate

solutions individually or in mixtures. Equally solutions of the preferred mixture can be diluted in many instances. More concentrated solution mixtures are envisaged but the solubility limit has to be born in
 5 mind.

The preferred solution above could typically range from a 30% solution to a 50% solution and the ratio of monosodium phosphate to dipotassium phosphate can be
 10 between 9 : 1 to 1 : 2 to create an effective gel.

A further feature of the invention envisages the use of the phosphate mixture as a powder to the ceramic grogs. Typically the addition of 3 - 7% by wgt. This mixture
 15 of grog and binder would be typically mixed with 120 - 160 ccs of water per Kg. of grog.

The slurry is made from a grog typically natural crushed magnesite or of sintered or of fused magnesite in mesh
 20 sizings

	60%	-1+½ mesh
	30%	-200 mesh
25	10%	-325 mesh fused magnesia or sintered magnesia

For extra strong moulds as described in 741,381 the

addition of

extra monosodium phosphate - 1-2%

extra dicalcium phosphate - 1-2%

5

may be added to the grogs as a powder or the mould can be strengthened as described by Shaw Process using phosphoric acid solution. The mixture is then in accordance with a preferred feature of the invention
10 mixed with polypropylene fibres typically 1-2% by wgt and typically 60 to 125 microns diameter 3 - 6 mm long. These fibres when melted away leave voids to achieve the desired porosity.

15 A very mobile slurry of this is prepared by adding the solution (available commercially as Clinochem 672 Bonding Solution). Typically between 120 ccs liquid to 160 ccs liquid solution per kilo of magnesia mix. When mixed, possibly vacuumed (as described in various Shaw Process
20 literature) the slurry is poured over a pattern in like manner to 716,394.

At 70°F this slurry will set in approximately 2 minutes. The setting time can be adjusted by reducing the fine
25 magnesia fractions and substituting typically sintered or fused spinel in like size and proportions. This will

increase the setting time or by substituting a less sintered fine magnesia in like quantity from the 200 or 300 mesh magnesia, typically magnesia (Lycal) by Redland Magnesia in order to shorten the gel time. After gelling
5 the mould is stripped. If the mould is then placed in an oven at 200°F or so (above boiling point of water and above melting point of polypropylene fibres) then surprisingly a stable mould permeable by virtue of discharged water and the voids left by the melted fibres
10 is formed without further need for heating. That is not to say that the mould could not be heated to 500 - 600°C as described in 741,381 but it is not necessary except if further strength to the mould is required.

15 Magnesia moulds (basic ceramics) are substantially more resistant to metal mould reactions than alumina silicates. The removal of silicates reduces reactions further. Thus an economical mould can be made without recourse to the problems outlined.

20

The polypropylene fibres generate permeability and permit rapid drying of the mould. The use of water based binder removes the need for volatiles which are expensive and a problem in respect of health and safety. Other
25 phosphates such as aluminium ortho phosphate, magnesium ortho phosphate, ammonium poly phosphates could be used

as variously described for example in EPA 0,501 662 and WO 94/21571. These binders however, do not remove satisfactorily the environmental problems even if they satisfy the technical problems.

5

It has further been found that very good moulds can be made for the process recently described as improvements of the above as follows.

10 The ceramic mixture Bauxite, Alumina or Zircon made with similar granulometry and using polypropylene fibres may be mixed with 2-10% Magnesia active and finely divided [for gel control] and

15 1. Dry powdered Monosodium Phosphate 1-4% and then adding as a liquid silica sol. 30-40% or

2. Premix into Monosodium Phosphate 50% w/v to Silica sol. at 20-30% SiO_2 and then using as a binder liquid as described originally in Shaw ethyl
20 silicate mixtures or

3. Preparing a solution of 50% w/w Monosodium Phosphate and mixing this solution 30-70% v/v with
25 30-40% Silica sol.

Slower setting times on even substantially basic ceramics such as fused or highly calcined Magnesia of the Alumina Magnesia Spinel may be used if instead of Monosodium phosphate a Dipotassium phosphate is used but then in a similar manner to 1, 2 and 3 above.

The advantage of this additional process is that very strong moulds can be made by simply drying the mould at between 150-250°C. Naturally it is beneficial to fire up to 650°C as previously described but only if it is a requirement of the rest of the process parameters - for example wax removal.

There are no hazardous or smell generating ingredients in the chemical binders and as before the polypropylene fibres are removed at temperatures as low as 200°C.

This system is particularly suited to lower melting point metals such as copper, bronze and aluminium. The presence of Sodium or Potassium is less noticeable than the previous examples since Silica sol. is a partial replacement.

The disadvantage is however that the Silica, Na/K and Magnesia form a low melting point eutectic. However the effect on lower melting point metals or alloys is

reasonably insignificant.

It is well known that many phosphates can be used to make refractory cements, mortars and bricks as well as
5 additives to improve castables all in the context of setting by a hydraulic reaction.

The most commonly used phosphates are aluminium ortho phosphates, sodium tripolyphosphate, sodium hexameta
10 phosphate and phosphoric acids.

Aluminium ortho phosphate and phosphoric acid are used extensively for aluminous silicate castables as well as cements, rammables and pressed shapes. Sodium
15 tripolyphosphate is used extensively as an addition to calcium aluminate cement castables for aluminas and aluminous silicates. Sodium hexameta phosphates are used for pressed brick including basic brick. In this specification cement is used to designate a hydraulically
20 settable material.

The present invention is not concerned with hydraulic setting but with systems wherein a settable magnesium phosphate is formed by chemical reaction. The set
25 magnesium phosphate is fired to yield magnesia.

EPA 0,501,662 designated P8 cites an instance where a reactive ammonium phosphate can be used in a practical manner for a range of magnesia - alumina spinels. It is recognised that the evolution of NH_4 is sometimes
5 limiting.

My WO 94/21571 designated P450 cites similarly a mixture of aluminium and magnesium phosphate can be used in a practical manner for magnesia - alumina spinels.

10

This Patent Application concerns castables and it concerns castables that are cement free and essentially very rich magnesia - magnesia alumina spinels.

15 Whilst sodium hexameta phosphates and potassium phosphates in generality are cited as suitable as binders for magnesia rich refractories as already mentioned above, these citations have not been made in the context of a gellable bonding systems.

20

The present invention envisages short chain molecules of sodium phosphate, potassium phosphate and calcium phosphate reacting to form gels that are usable in castables of very high magnesia content.

25

This is contrary to the generally recognised uses of

these phosphates in ceramics and refractories. Moreover these phosphates used individually whilst gelling and forming solid green shapes in the presence of magnesia form relatively weak pieces with no great inherent strength, except perhaps by adding unacceptably high amounts of phosphates - 10% or more x wgt.

What I have found is that:

1. The short chain mono sodium phosphate [an acidic phosphate ph 4.5] when combined with a short chain potassium phosphate, dipotassium phosphate [a basic phosphate ph 9] will form a gel with magnesia in a controlled manner and further build up quickly a green strength comparable to aluminium phosphates or say cements based on calcium aluminate.

2. The short chain monosodium phosphate has a similar effect with hexameta phosphate [also basic ph 7.5] which is surprising since hexameta phosphate normally is very slow reacting with basic magnesia refractories and too slow for practical purposes.

3. The short chain monosodium phosphate has a similar effect with dicalcium phosphate [which is surprising since dicalcium phosphate is insoluble with water and thus has a negligible reaction with magnesia]. It is

worth noting that the best result appears to be a combination of an acidic soluble phosphate with a basic phosphate. Thus

- 5 4. The short chain mono sodium phosphate will have a similar effect in presence of the poly ammonium phosphates. However, if a polyammonium phosphate is acceptable within a system our co-pending Patent [P8] offers a solution.

10

A preferred mixture is:

- | | | |
|----|-----------------------|----------------|
| A. | Monosodium phosphate | 3 parts x wgt. |
| | Dipotassium phosphate | 2 parts x wgt. |
- giving a resultant ph of approximately neutral 7.

15

The converse is:

- | | | |
|----|---------------------------|------------------------|
| B. | Monopotassium phosphate | 3 parts [acid ph 4.5] |
| | Sodium hexameta phosphate | 3 parts [basic ph 7.5] |
- giving a mixed ph of approximately 7. This mixture is
 20 however much slower to build up strength after gellation
 and tests have shown it not as effective as A.

The other preferred mixture is:

- | | | |
|----|----------------------|---------|
| C. | Monosodium phosphate | 3 parts |
| 25 | Dicalcium phosphate | 2 parts |
- to again give a mixed ph of approximately 7.

Monocalcium phosphate it is found reacts quickly with basic mixtures of magnesia. It like the other mono compounds cited above is acid. It was found that a mixture of it with dicalcium phosphate was not as effective as A, B, C, probably for the reason that monocalcium phosphate has only a limited solubility in water. The selection of phosphate is governed to a notable extent upon the solubility of the phosphate concerned. Clearly an insoluble or only slightly soluble phosphate not only takes longer to disperse or dissolve in water and thus react with magnesia but then results in a much weaker green strength.

Our preferred mixture for maximum general performance - that is to say:

- a) a controlled setting time within the acceptable limits of time, 10 mins to 2 hours.
- b) good green strength and maximum fired strength for given phosphate content
- c) good strength build up after initial set so that a castable can be readily stripped from its mould
- d) lacking any hazardous or offensive by-products on

heating is

D.	Monosodium phosphate	3 parts
	Dipotassium phosphate	1 part
	Dicalcium phosphate	1 part

5 though this is not intended as restrictive.

If the presence of calcium is undesirable in the ultimate refractory then mixtures A or B would be preferred.

10 By way of example the following is cited as a mixture for the manufacture of a refractory castable.

Aggregates as follows are all mixed together properly

15	Magnesite dead burnt or pericluse	-5+3 mesh	35 parts x wgt.
		-3+1	20
		-1	20
20	Fused magnesia (pericluse)	-200	15
	Sintered Magnesia	-200	5
	Fused Magnesia	-300	5
25	to which are mixed		
	Monosodium phosphate		3
	Dipotassium phosphate		1
	Dicalcium phosphate		1

30 Water is added - between 4-8% by wgt. to form a slurry

which can be cast into a mould and vibrated to consolidate and left and allowed to set. This mixture, depending upon the temperature and the fineness of the -200 and -300 mesh magnesia will set typically at 18°C in about 20 minutes.

A particular example of a castable readily available from Clinochem Limited is as follows:-

10 Clinochem cement Free Basic Castable having a chemistry:

	MgO	80%
	Al ² O ³	13%
	CaO	0.9%
	P ² O ⁵	3.85%
15	Fe ² O ³	0.05%
	Na ² O	1.35%
	K ² O	0.90%

This being a magnesia - magnesia spinel mixture gives physical properties as

20	Bulk density	2.75 gm/cc
	% Porosity	19%
	Cold Crush mpa	45
	Cold MOR mpa	10
	RUL @ 1500	less than 3%
25	Refractoriness	greater than Cone 38 [Segar]
	Thermal Shock	greater than 100

The results are obtained on cast bricks 8 x 4 x 2", cast after mixing with 65 ccs H²O per kilogram of castable in a high sheer mixer and vibration cast for 3 minutes. The setting time of the castable to strip being 90 minutes.

5 The binder system consisted of an addition of 7% of preferred mixture D.

The following phosphates all to differing extents can be induced to form a gel in presence of magnesia. Thus
10 enabling them to be used as non-cement castable.

15	Sodium Phosphates	Monosodium phosphate	
		Disodium phosphate	
		Trisodium phosphate	
		Tetrasodium phosphate	
		Sodium Hexameta phosphate	
20	Potassium phosphates	Mono potassium phosphate	MKP
		Di potassium phosphate	DKP
		Tri potassium phosphate	TKP
		Poly potassium phosphate	TKPP
	Calcium phosphates	Mono calcium phosphate	
		Di calcium phosphate	

This is despite them having widely differing solubility from nil to 100% and ph values acid and base.

25

The reaction in every case one has to presume is the

formation of insoluble magnesium phosphate.

Short simple molecular structures work fastest to form a gel. The use of Calgon [sodium hexameta phosphate] is cited in many places as being a suitable binder for refractories to be pressed or as a heat setting or a setting cement with many refractory materials including basic materials such as magnesite. No mention is made of its ability to be used as a castable system which sets in presence of magnesia. This could be because in practice it takes several days to set. However, the use of monosodium phosphate has not to my knowledge noted anywhere. This being the shortest chain of the sodium phosphates reacts the fastest to set in presence of magnesia.

In the presence of a magnesia body typically

	Magnesia Sintered	-3+1 mesh	55% x wgt
	Sintered	-1	20% x wgt
20	Sintered	-200	20% x wgt
	Fused	-325	5% x wgt

will set and form a hard refractory within 1 - 2 minutes at 70°F. If fused -200 mesh is used it will set in about 5 - 10 minutes at 70°F.

That calcium phosphates are effective is even more

surprising because:

- a) one would not expect calcium to pass its phosphate atoms to magnesium since magnesium is lower on the periodic table.
- b) Mono calcium phosphate has only limited solubility in water and dicalcium is not soluble at all in water.
- 10 Mono potassium phosphate reacts in a close approximation to monosodium phosphate in presence of magnesia as does mono calcium phosphate. Trisodium phosphate has been proposed as an additive and binder for cement castables. It is not cited as a binder in the absence of cement.
- 15 The binder in these instances appears always to refer to the effect of phosphate as an intermediate binder for calcium aluminate when heated above 650°C , not as a means of making a green shape.
- 20 What is also surprising is that the combination of sodium hexameta phosphate with aluminium tripoly phosphate results in not only a gel which is harder than sodium hexameta phosphate but that in presence of magnesia the two combined set in about 2 hours at 60°F and are very
- 25 hard in 4-5 hours at that temperature.

Sodium hexameta phosphate is very slow to react with magnesia - on its own several days. It has a ph of 7 and is very soluble in water or phosphoric acid and on its own has a negligible reaction with magnesia.

5

It is further surprising that potassium tetra polyphosphate behaves in a similar manner to the above in conjunction with aluminium tripolyphosphate.

10 The preferred mixture is using the sodium phosphate in a ratio of approximately 3 sodium to 1 aluminium. However, this is not intended to be restrictive since different refractory applications could easily find expedient to change the ratio.

15

I have discovered that by combining one or more of these unlikely phosphates a result can be obtained which generates castable gels over a wide range of temperatures and over a wide range of magnesia content giving results
20 that compare favourably with calcium aluminate cements at one end of the spectrum to a water based binder that compares very favourably with ethyl silicate at the other.

CLAIMS

1. A method of manufacturing moulds which comprises the steps of mixing a settable slurry of one or more phosphates and a suitable refractory aggregate and incorporating fibres into the slurry which, when melted after setting define stabilising voids.
5
2. A method as claimed in claim 1 wherein the slurry is based on a substantially neutral solution containing principally monosodium phosphate.
10
3. A method as claimed in either claim 1 or claim 2 wherein the fibres are of polypropylene.
15
4. A method of making a refractory object which uses a magnesia/phosphate setting system wherein the phosphate is a short chain sodium, potassium, or calcium or equivalent phosphate.
20
5. Methods as claimed in either claim 1 or claim 4 and substantially as described in the specification.
6. Objects produced by a method according to any preceding claim.
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- 20 -

**The
Patent
Office**

Application No: GB 9520669.4
Claims searched: 1-3

Examiner: J P Leighton
Date of search: 17 January 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): B5A(AC, AM5X, AND, ANX, AT3P)
Int CI (Ed.6): B28B(1/00, 1/14, 1/52); B22C(9/00, 9/06); B22D(7/06, 7/08, 7/10)
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 1410634 A I C I Ltd	
A	GB 1402318 A Foseco International Ltd.	
A	GB 0644994 A Emerik Imre Valyi	
A	US 4623014 A Giulini Chemie GmbH	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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